Electrochemical Properties of Cellulose Acetate Membranes in Aqueous Electrolyte Solutions Containing Hydrophobic Ions (Commemoration Issue Dedicated to Professor Tetsuya HANAI On the Occasion of His Retirement)

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Electrochemical Properties of Cellulose Acetate Membranes in Aqueous Electrolyte Solutions Containing Hydrophobic Ions.

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Voltage-Current (V-I) characteristics and ac impedance were measured for the cell system composed of cellulose acetate (CA) membranes separating two NaCl solutions, one side containing a small amount of Tetraphenyl borate (TPB^-) and the other Tetraphenyl arsonium ($TPAs^+$). The rectification effect on the V-I characteristics and the associated dielectric relaxation were found. The membrane capacitance and conductance of the cell system depend on frequency. The limiting values of the membrane capacitance at high frequencies are independent of the applied bias voltage, being considered to be the geometric membrane capacitance. While the limiting values of the membrane capacitance and conductance at low frequencies depend on the applied bias voltage. Dependence of the values on the applied bias voltage and the rectification effect are discussed on the basis of a bipolar membrane model which consist of two abutting region of oppositely charged layers in series. In conclusion, it is considered that the large hydrophobic ions are specifically adsorbed in the CA membrane and show some behavior as fixed charges.

KEY WORDS: Voltage-current characteristics / Dielectric relaxation / Cellulose acetate membrane / Hydrophobic ions / Space charge.

1. INTRODUCTION

In a previous paper[1], dielectric properties were reported of cellulose acetate (CA) membranes in aqueous electrolyte solutions. The membrane capacitance and conductance of the CA membranes in aqueous solutions were evaluated from the experimental results by means of the dielectric analysis.

For the system composed of the CA membranes separating two electrolyte solutions containing hydrophilic ions, the only dielectric relaxation due to the geometric capacitance and conductance of the membrane was observed. It is important to learn the dielectric behavior of the membranes in the ambient aqueous solution containing hydrophobic ions. For instance, it is known that a small amount of hydrophobic ion in the ambient aqueous solutions greatly affects the dielectric behavior of lipid bilayer membranes [2,3].

This paper describes electrochemical properties of the cellulose acetate membrane separating two NaCl solutions, one side containing a small amount of hydrophobic anion and the other hydrophobic cation. The rectification effect on voltage-current (V-I) characteristics and the associated dielectric relaxation were observed for this cell system. By the analysis of the relaxations, the membrane capacitance and conductance were evaluated, showing the dependence on frequency and applied bias voltage.

These properties were studied for bipolar membranes immersed in electrolyte

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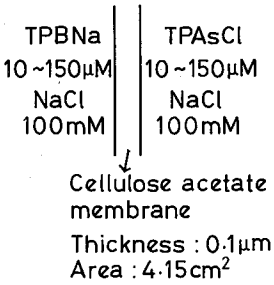


Fig. 1 The system studied.

solutions, both theoretically and experimentally[4-8]. Bipolar membranes consist of two abutting regions of fixed charges in series, one layer being cation-selective and the other anion-selective. They have attracted interest for an industrial application of ion exchange membranes and explaining some of the electrical characteristics of biological membranes. The phenomena observed in the present system are discussed on the basis of the bipolar membrane model.

2. EXPERIMENTAL

The system studied is shown in Fig. 1. It consists of a cellulose acetate membrane separating two 100mM NaCl aqueous solutions, one side containing Sodium Tetraphenyl borate (TPBNa) and the other Tetraphenyl arsonium chloride (TPAsCl) of concentrations 10-150μM.

The cellulose acetate membranes were prepared by slowly withdrawing a clean glass plate from a 3wt% acetone solution of cellulose acetate (E398-3 Eastman Codak Co., Ltd.) and evaporating a solvent completely[9]. The thickness of the membrane t was estimated to be about 0.1μm by the following equation[10]:

$$t=0.4\left(\frac{\rho_l}{\rho_s}\right)w_s\sqrt{\frac{\mu u_0}{\rho_l g}}, \tag{1}$$

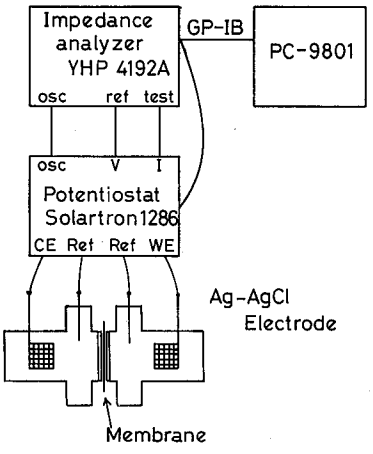


Fig. 2(a)

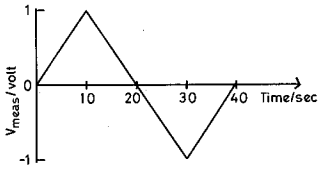


Fig. 2(b)

Fig. 2 (a) The measuring system for voltage-current characteristics and ac impedance.

(b) The triangular voltage applied to the cell system for measuring voltage-current characteristics.

where ρ_l and ρ_s the density of the solution and cellulose acetate, respectively, w_s the weight fraction of the cellulose acetate in solution, μ the viscosity of solution, u_o the withdrawal rate, and g the gravitational constant.

The measuring system for the V-I characteristics and dielectric measurement is shown in Fig. 2(a). The cell system consists of a four electrode configuration. The two inner electrodes were used to measure the potential difference and the outer electrodes to pass and measure the current through the membrane. All electrodes were Ag wire or mesh coated with AgCl.

The V-I characteristics were measured with Solartron 1286 Potentiostat. The triangular voltage as shown in Fig. 2(b) was applied to the cell system. The sweep rate was 100mV/sec. The electrode immersed in solution containing $TPAs^+$ ion was used as a reference. In this paper, the positive bias voltage is called "forward" and the negative bias voltage "reverse".

The dielectric measurements were carried out with 1286 potentiostat and Yokogawa Hewlett Packard 4192A LF Impedance Analyzer operating in a frequency range between 5Hz and 74kHz at each applied bias voltage. A 28mV peak-to-peak ac voltage was applied to the cell system for impedance measurement. All measurements were carried out at room temperature 25°C.

3. RESULTS AND DISCUSSION

3.1. Voltage-Current Characteristics

Figure 3 shows the V-I characteristics of the cell system shown in Fig. 1. The voltage V_{dc} was applied to the membrane, beign obtained from the measuring voltage V_{meas} by

$$V_{dc} = V_{meas} - I_{dc}R_s \tag{2}$$

where I_{dc} the measuring current through the membrane and R_s the solution resistance between the two electrodes and the CA membrane. The resistance R_s was determined

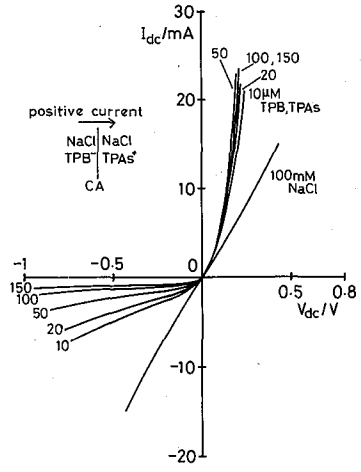


Fig. 3 The voltage-current characteristics of the cell system shown in Fig. 1 and in the absence of the hydrophobic ions.

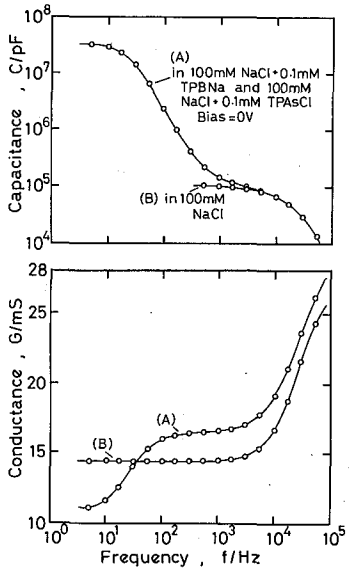


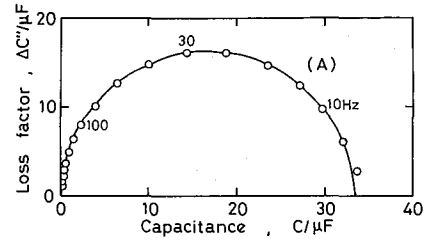
Fig. 4 Frequency dependence of the capacitance C and the conductance G observed for the cell system in the presence of the hydrophobic ions (A) and in the absence of the hydrophobic ions (B). An applied bias voltage is 0V.

by the ac impedance measurement which will be described later.

The rectification effect is clearly observed for the cell system composed of the CA membrane separating the electrolyte solutions containing the hydrophobic ions, while it is not observed for the membrane immersed in a 100mM NaCl solution. The reverse current decreases with increasing the concentration of the hydrophobic ions.

3.2. Dielectric Properties

Figure 4 shows the frequency dependence of the capacitance C and the conductan-



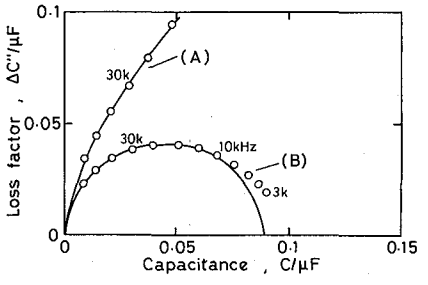


Fig. 5(a)

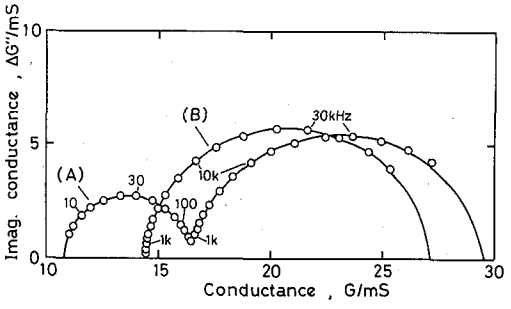


Fig. 5(b)

Fig. 5 Complex plane plots of the complex capacitance (a) and the complex conductance (b) of the same data as shown in Fig. 4.

ce G observed for the cell system composed of the CA membrane immersed in a 100mM NaCl solution (B) and that containing the hydrophobic ions (A) when the applied bias voltage is 0V. In the case of (B), only one dielectric relaxation is observed, being considered to be due to the interfacial polarization between the membrane and the ambient aqueous solutions. In the case of (A), a large low frequency dielectric relaxation is observed in addition to the high frequency relaxation. The complex plane plots of the same data are shown in Fig. 5. In the former case, one semicircle is observed, while two semicircles are observed in the latter.

The membrane capacitance C_{ft} and conductance G_{ft} are obtained by the following equation[1]:

$$\frac{1}{C_{ft}+G_{ft}/j\omega}=\frac{1}{C+G/j\omega}-\frac{1}{C_w+G_w/j\omega}, \tag{3}$$

where j the imaginary unit, ω the angular frequency and C_w and G_w are the capacitance and conductance of the ambient aqueous solution, respectively. The values of C_w, G_w are estimated by means of the extrapolation of the complex plane plots to the high frequency limit. The solution resistance R_s is obtained by $R_s=1/G_w$.

The complex plane plots of the membrane capacitance and conductance are shown in Fig. 6. One semicircle is clearly observed. For the analysis of the results, we adopt the equivalent circuit as shown in Fig. 7.

The value of the geometric capacitance C_f is about $0.1\mu F/cm^2$, being obtained as the limiting value of the capacitance C_{ft} at high frequencies. The C_f-value does not

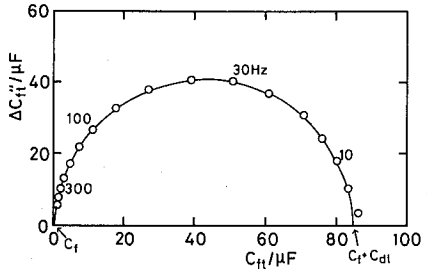


Fig. 6(a)

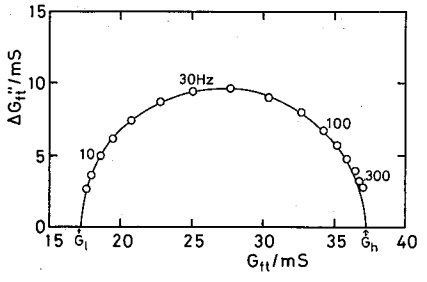


Fig. 6(b)

Fig. 6. Complex plane plots of the complex membrane capacitance C_{ft}^* (a) and the complex membrane conductance G_{ft}^* (b), which were calculated by Eq. 3 from the data shown in Fig. 4(A).

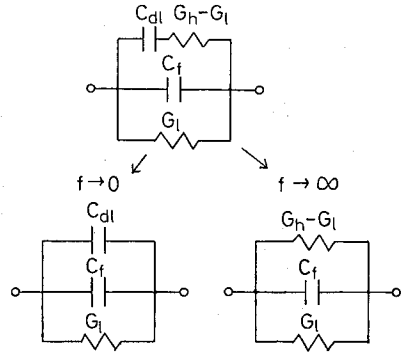


Fig. 7. The equivalent circuit model for simulating the frequency dependence of the membrane impedance as shown in Fig. 6.

depend on the applied bias voltage and the concentrations of the hydrophobic ions and NaCl. The membrane thickness t can be estimated to be about 0.1μm by the following equation:

$$t=\frac{\epsilon_v \epsilon_f}{C_f}, \tag{4}$$

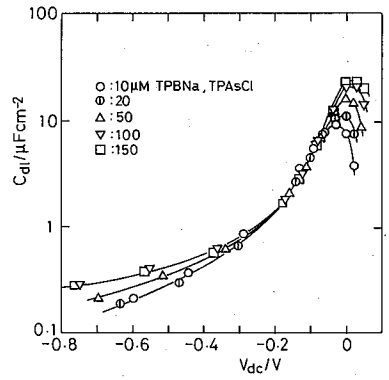


Fig. 8.

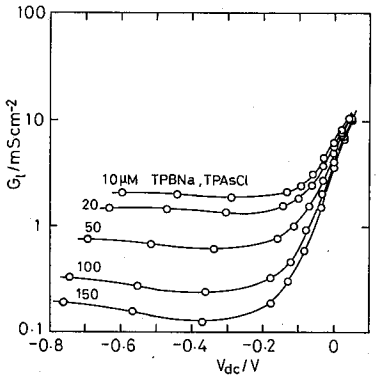


Fig. 9.

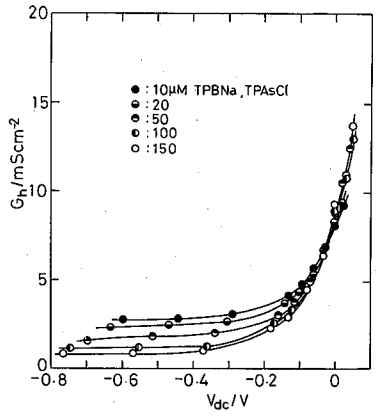


Fig. 10.

Fig. 8, 9, 10. Dependence of the capacitance C_{dl} (Fig. 8) and the conductances G_l (Fig. 9), G_h (Fig. 10) on the applied bias voltage V_{dc}.

where $\varepsilon_f=15$ the relative permittivity of the CA membrane in aqueous solution and ϵ_v the permittivity of vacuum. The estimated value of the membrane thickness from the dielectric method agrees with the estimated value by Eq. 1.

The values of the capacitance C_{dl} and the conductances G_l, G_h depend on the applied bias voltage and the concentrations of the hydrophobic ions as shown in Figs. 8-10.

In the present paper, the case is discussed of the reverse bias voltage. When the forward bias voltage was applied, the frequency dependence of the capacitance and conductance was found to be inductive at low frequencies. This phenomenon is still under consideration.

The values of C_{dl} are 0.1-30μF/cm^2, which are large compared with the ordinary geometric capacitance. They increase with increasing the concentration of the hydrophobic ions and the appllied bias voltage. They also increase with increasing the NaCl concentration as shown in Fig. 11. This capacitance appears to be attributed to the space charge layer.

The conductances G_l, G_h increase as the increase in the applied bias voltage and the NaCl concentration and as the decrease in the concentration of the hydrophobic ions as shown in Figs. 9, 10, 12. The conductance G_l is the limiting value of the membrane conductance G_{ft} at low frequencies. It is considered to be obtained by differentiating the current I_{dc} with respect to the voltage V_{dc} at each bias voltage. The conductance G_h is the limiting value at high frequencies. It must be directly related to the concentration c_i and mobility u_i of the mobile ion i in the membrane by the following equation:

$$G_h=\sum_i \frac{1}{\int_0^t \frac{dx}{Fz_iu_ic_i}}, \tag{5}$$

where z_i the elementary charge of the mobile ion i and F the Faraday constant. Hence,

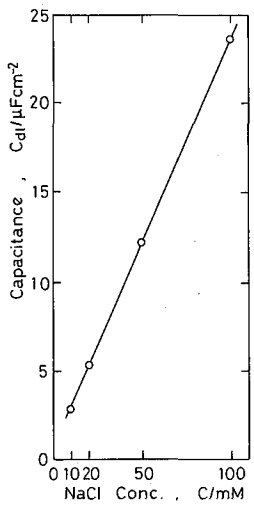


Fig. 11.

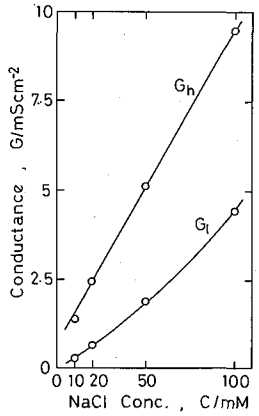


Fig. 12.

Fig. 11, 12. Dependence of the capacitance C_{dl} (Fig. 11) and the conductances G_l, G_h (Fig. 12) on the NaCl concentration of the ambient aqueous solution. The value of the concentration of TPB^-, $TPAs^+$ ions is 100μM and the applied bias voltage is 0V.

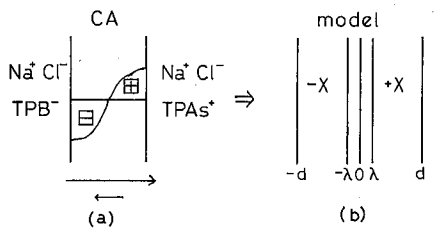


Fig. 13. (a) The membrane model of the CA mambrane which adsorbs TPB^- ion from the left side of the aqueous solution and $TPAs^+$ ions from the right.
(b) The simplest bipolar membrane model.

it is infered that the total concentration of the mobile ions in the membrane decreases with decreasing the applied bias voltage V_{dc}.

3.3. Theoretical Consideration

The phenomena observed for the present system were very similar to those for the bipolar membrane[4-8]. It is considered that the large hydrophobic ions TPB^-, $TPAs^+$ are specifically adsorbed in the hydrophobic CA membrane. The adsorbed hydrophobic ions behave as the fixed charges since their mobilities in the membrane are considered to be very small compared to Sodium and Chloride ions. Hence, the CA membrane in the present system is considered to be the bipolar membrane as shown in Fig. 13(a). Following Mauro[4] and Coster[6], the simplest bipolar membrane model as depicted in Fig. 13(b) is discussed.

The bipolar membrane extends from $x=-d$ to $x=d$. The region between $x=-d$ and $x=0$ has negative fixed charges, while that between $x=0$ and $x=d$ has positive fixed charges. The fixed charge densities of the positive and negative regions are X and $-X$, respectively. In the transition region between $x=-\lambda$ and $x=\lambda$, there are no mobile charges. The region of the negative space charge extends from $x=-\lambda$ to $x=0$ and that of the positive space charge extends form $x=0$ to $x=\lambda$.

By solving the Poisson equation, the thickness of the space charge region λ is obtained by the following equation:

$$\lambda=\sqrt{\frac{\varepsilon_v\varepsilon_f V_{junc}}{FX}}, \tag{6}$$

where V_{junc} the potential difference between $x=-\lambda$ and $x=\lambda$. The value of V_{junc} is the sum of the Donnan potential difference between the oppositely charged layers $2\Psi_0$ and the applied bias voltage $-V_{dc}$, that is

$$V_{junc}=2\Psi_0-V_{dc}. \tag{7}$$

Here it is assumed that the bias voltage is applied to the transition region only.

The Donnan potential Ψ_0 is

$$\Psi_0=-\frac{RT}{F}\,ln\left\{\frac{1}{KC_0}\left(\sqrt{\left(\frac{X}{2}\right)^2+(KC_0)^2}-\frac{X}{2}\right)\right\} \tag{8}$$

where K the partition coefficient of NaCl between the membrane and aqueous solution, c_0 the NaCl concentration of solution and F, R, T are the usual meanings.

The direct current I_{dc} is the diffusion current of the co-ions in each fixed charge region. Hence, the current per unit area I_{dc} is given by

$$I_{dc}=FD_{+}\frac{c_{+p}(\lambda)-c_{+p}(\mathrm{d})}{\mathrm{d}-\lambda}+FD_{-}\frac{c_{-n}(-\lambda)-c_{-n}(-\mathrm{d})}{\mathrm{d}-\lambda}, \tag{9}$$

where D_{+}, D_{-} the diffusion coefficients of Na^{+}, Cl^{-} ions at x, respectively.

The concentrations $c_{+p}(\mathrm{d})$, $c_{-n}(-\mathrm{d})$ are not affected by the applied bias voltage. Using the Maxwell-Boltzmann distribution law, they are given by

$$c_{+p}(\mathrm{d})=c_{-n}(-\mathrm{d})=Kc_0\exp(-\frac{F}{RT}\Psi_0). \tag{10}$$

The concentrations $c_{+p}(\lambda)$, $c_{-n}(-\lambda)$ depend on the applied bias voltage V_{dc}. They are given by

$$c_{+p}(\lambda)=c_{-p}(-\lambda)=Kc_0\exp(-\frac{F}{RT}\Psi_0)\exp(\frac{FV_{dc}}{RT}). \tag{11}$$

Substituting Eqs. 10 and 11 into Eq. 9, the current I_{dc} is expressed as the following equation:

$$I_{dc}=FKc_0\exp(-\frac{F}{RT}\Psi_0)\frac{D_{+}+D_{-}}{d-\lambda}(\exp(\frac{FV_{dc}}{RT})-1). \tag{12}$$

The conductance G_1 can be obtained by differentiating I_{dc} with respect to V_{dc}, that is

$$G_1=\frac{\mathrm{d}I_{dc}}{\mathrm{d}V_{dc}}. \tag{13}$$

The capacitance C_{dl} is considered to be attributed to the storage of charge in the transition region. From Eq. 6, we have

$$V_{junc}=\frac{FX\lambda^2}{\epsilon_v\varepsilon_f}. \tag{14}$$

If the voltage V_{junc} increases by a small amount of δV, the width of the transition region increases by $\delta\lambda$. From Eq. 14, $\delta\lambda$ is given by

$$\delta\lambda=\frac{\epsilon_v\varepsilon_f\delta V}{2FX\lambda}. \tag{15}$$

As the increase in the width of the transition region, an amount of the space charge in the transition region increases by δQ. Hence, we have

$$\delta Q=FX\delta\lambda=\frac{\epsilon_v\varepsilon_f}{2\lambda}\delta V. \tag{16}$$

But the differential capacitance C_{dl} is defined as

$$C_{dl}=\frac{\delta Q}{\delta V}. \tag{17}$$

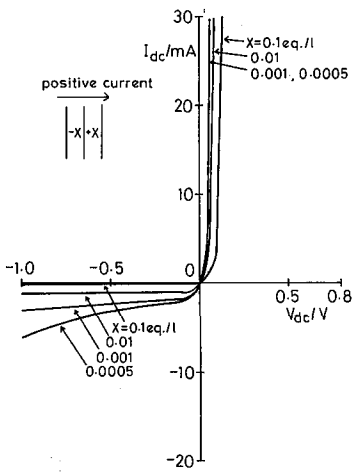
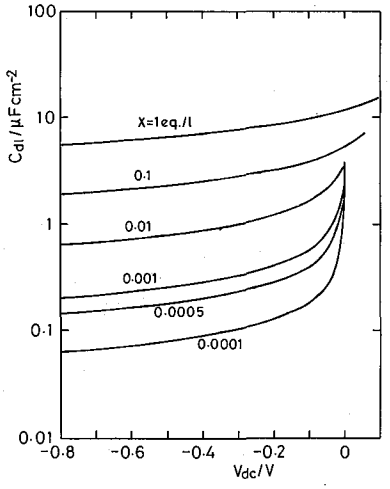


Fig. 14.



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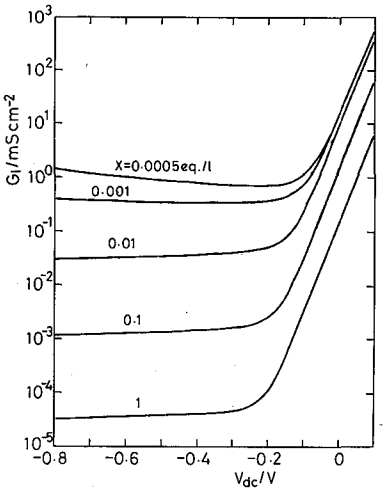

Fig. 16.

Fig. 14, 15, 16. Theoretical curves of the voltage-current characteristics (Fig. 14) and dependence of the capacitance C_{dl} (Fig. 15) and the conductance G_l (Fig. 16) on the applied bias voltage V_{dc}. The parameters adopted for the calculation are c_0=0.1M, K=0.1, $D_+ + D_- = 2.74\times10^{-9}$cm^2/sec, ε_f=15, T=298.15K and d=0.07μm. The current is the value per the membrane area 4.15cm^2

Hence, the capacitance per unit area C_{dl} is expressed by the simple equation as follows:

$$C_{dl}=\frac{\epsilon_v\varepsilon_f}{2\lambda}. \tag{18}$$

Theoretical curves of I_{dc}, G_l, C_{dl} against V_{dc} calculated by Eqs. 12, 13, 18 are depicted in Figs. 14, 15, 16. The features of the results are as follows. The current I_{dc} flowing from the positive charge region to the negative charge region is suppressed, whose direction is called "reverse". The reverse current decreases with increasing the fixed charge density X. The values of G_l, C_{dl} decrease with increasing the absolute value of the reverse voltage V_{dc}. As the increase in the fixed charge density X, the value of C_{dl} increases while the value of G_l decreases. The value of C_{dl} is 0.1-10μF/cm^2. These features agree with the experimental results. Quantitatively, the agreement between the theoretical calculations and the experimental results is poor. Probably, the reason for this is attributed to many assumptions of the bipolar membrane model.

In conclusion, it can be considered that the large hydrophobic ions are specifically adsorbed in the CA membrane and they behave as fixed charges. Hence, the CA membrane in the cell system shown in Fig. 1 behaves as the bipolar membrane.

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